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PRELIMINARY IRRADIATIONS OF PuC AND UC-PuC

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J. H. Kittel, L. A. Neimark, R. Carlander,
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ARGONNE NATIONAL LABORATORY
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ABSTRACT

Preliminary irradiations were made of arc-cast specimens of PuC and UC-PuC and of pressed and sintered pellets of UC-PuC to determine the suitability of these materials for further development as possible fuels for liquid metal-cooled fast reactors. The PuC content in the mixed-carbide specimens was near 20 w/o. The specimens were irradiated as fuel rods in the fast reactor EBR-I. Maximum fuel burnup and temperature during irradiation were respectively 0.10 metal atom percent and 650°C. The cast PuC specimens were found to have fractured to a greater extent under irradiation than did the cast mixed-carbide specimens. Dimensional changes in those specimens which did not fracture were negligible. Fission gas release from the cast specimens was 0.24% of the theoretical yield. The pressed and sintered pellets did not fracture under irradiation and showed negligible dimensional changes. Fission gas release from the pellets was 12.0% of theoretical. The high gas release from the pressed and sintered specimens is attributed to a relatively high degree of open porosity which existed in the pellets.

INTRODUCTION

Early work on the properties of UC[1-3] had shown that this compound was a promising fuel material for liquid metal-cooled reactors. It had also been determined that PuC possessed the same crystal structure (NaCl-type) as UC, so that PuC and solid solutions of UC-PuC were also of interest as possible fuel materials. PuC is of particular interest as a fuel for fast reactors in which a minimum core size must be combined with a high power density. UC-PuC mixtures are particularly of interest as high-temperature ceramic fuel for fast breeder reactors in which the relatively high thermal conductivity and high metal atom density of the carbide is a distinct advantage compared with the mixed oxide fuel UO_2-PuO_2.

Preparations were begun at Argonne National Laboratory in 1958 to determine the effects of irradiation on prototype fuel elements containing PuC and mixtures of UC and PuC. Preliminary irradiations in the EBR-I reactor have been completed and are described in this report.

EXPERIMENTAL MATERIALS AND PROCEDURE

Preparation of Specimens

For convenience, the specimens will be referred to as PuC or UC-PuC, although stoichiometric monocarbide compositions were not prepared in all cases.

Two fabrication methods were used to prepare experimental specimens. Arc-casting was used for both PuC and UC-PuC mixtures, and pressed and sintered pellets were made of UC-PuC mixtures. The nominal PuC content was 20 w/o in both types of UC-PuC compositions. The uranium in all UC-PuC specimens was enriched approximately 93% in U^{235} to enhance the rate of metal atom burnup.

The cast specimens of PuC and UC-PuC were prepared by arc melting and casting in an interchangeable hearth arc furnace. Pieces of carbon, plutonium, and/or uranium were directly alloyed into buttons by arc melting in a water-cooled copper crucible under a protective atmosphere of helium or argon. An alloyed button of about 35 g was then placed over the opening of a graphite tube mold. The button was heated by the arc and, when it was fully molten, dropped into the mold. The arc furnace was immediately evacuated to slow cool the casting. Flanged graphite molds were used for the UC-PuC specimens. The molten PuC alloys reacted with the graphite flange; therefore, they were melted on a cooled copper surface and cast into a graphite sleeve mold. Fuel pins of the PuC composition were easier to cast and had a better surface appearance than those of UC-PuC. This behavior was attributed to the greater superheat of the PuC melt prior to casting due to its lower melting point of 1650°C compared with that of about 2300°C for UC-20 w/o PuC.

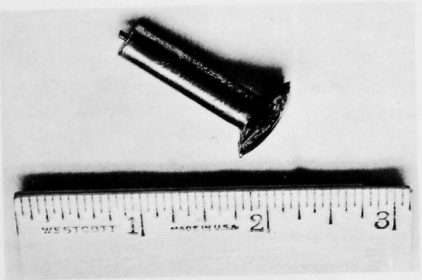

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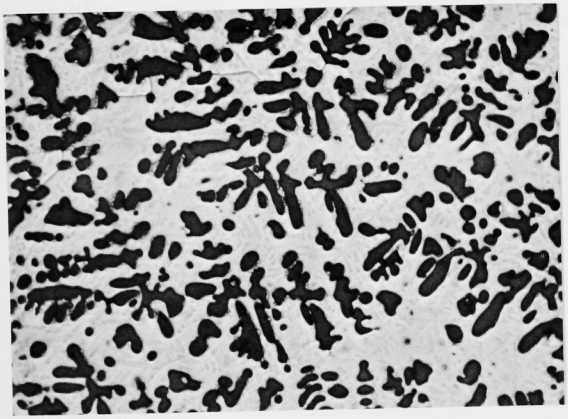
Figure 1. Typical Arc-cast PuC Specimen before Machining to Size

The tops of the castings were removed, leaving fuel pins about 25 mm (1 in.) long by 7.6 mm (0.30 in.) in diameter. Unsuccessful attempts were made to cast the specimens with an axial hole for accommodation of a central thermocouple. Eight cast PuC and eight cast UC-PuC fuel pins were made. A typical casting before removal of the top is shown in Figure 1. All of the specimens had densities greater than 98% of theoretical.

The carbon contents of the cast specimens were varied from 4.75 to 5.73 w/o. The plutonium contents in the cast mixed-carbide specimens were varied from 17.2 to 27.8 w/o. Typical microstructures are shown in Figures 2 and 3. More

detailed descriptions of the preparation and properties of arc-cast plutonium carbides have been published elsewhere.[4,5] Most of the specimens were purposely made with excess carbon over that required for stoichiometric monocarbide in order to avoid the possible presence of a free plutonium phase which could cause rapid penetration of the stainless steel cladding. A second phase distribution of sesquicarbide was present in the hyperstoichiometric material. Interpretation of the cast microstructures was aided by information obtained by S. Rosen and associates.[6]



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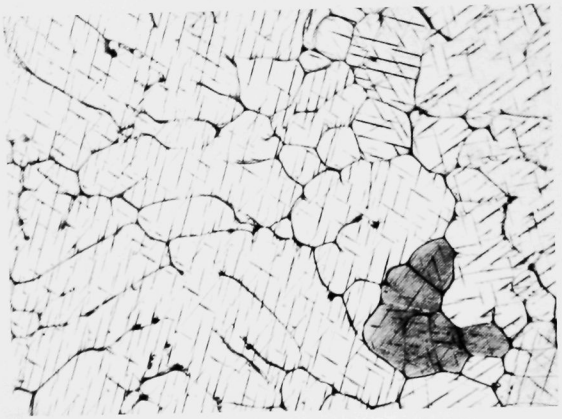
200X

Figure 2

Primary Pu_2C_3 (Dark) in a PuC Matrix of an As-cast Pu-50.4 a/o C alloy



31683

500X

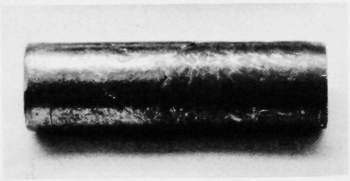
Figure 3

Windmanstätten Precipitate (Intersecting Planes) of (U, Pu)$_2C_3$ in a (U, Pu)C Matrix of an As-cast (U, 20 Pu)-50.5 a/o C Alloy

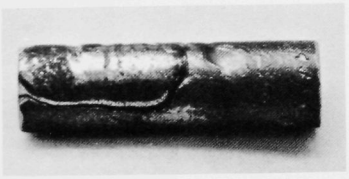
The UC used in the pressed and sintered specimens of UC-20 w/o PuC was made by reacting pellets of enriched UO_2 and carbon under vacuum in a UC-lined graphite crucible at 1600°C. The PuC was made by reacting

pellets of PuO_2 and carbon, with Carbowax as a binder, at 1300°C under vacuum in a tantalum-resistor furnace. The UC and PuC clinkers were ground together in the desired weight ratio and cold-pressed into right cylinders with an axial thermocouple hole. The cylinders were then fired under vacuum at 1650°C from 1 to 4 hr in a tantalum-resistor furnace. A total of 15 pressed and sintered specimens were prepared. The average bulk density was 55.1% of theoretical. Typical final dimensions of the pellets were 7.92 mm (0.312 in.) diameter by 15 mm (0.60 in.) long.

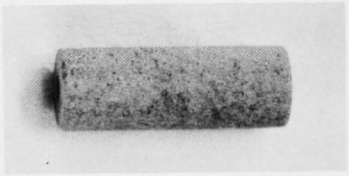
Typical specimens of all three types are shown before irradiation in Figure 4.



PuC (Arc-cast)



UC-20 PuC (Arc-cast)



UC-20 PuC (Pressed and Sintered)

106-5470

2X

Figure 4. Typical Specimens before Irradiation

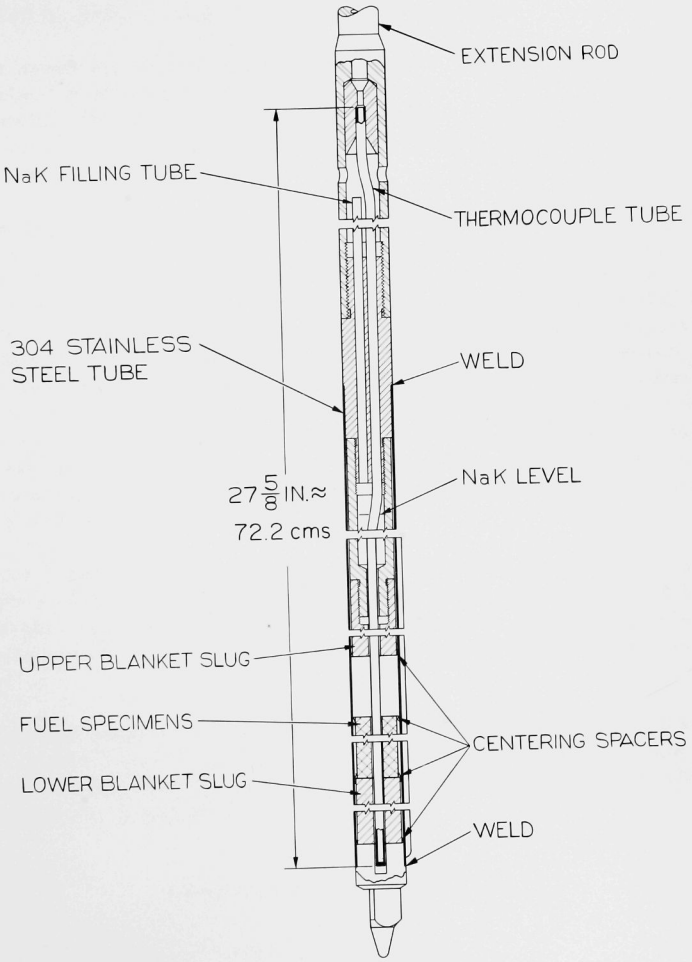
Irradiation of Specimens

The EBR-I reactor was used for the irradiations. Although this reactor has a relatively low rate of fuel burnup, this was not considered to be a serious disadvantage, since high burnup was not an objective in the preliminary tests. The reactor was selected mainly because its fast flux would enable uniform burnup to be achieved in PuC specimens of reasonable size.

At the time the irradiations were made, the EBR-I reactor contained the Mark III core. The fuel elements in this core were rods 10.3 mm (0.404 in.) in diameter.[7] It was desired to irradiate the carbide specimens directly in the core of the reactor. The specimens were therefore

placed in three special fuel rods having outer dimensions and end fittings identical to the Mark III fuel rods. These special fuel rods were interchangeable with existing rods in the Mark III core.

A drawing of the assembled special fuel rod, M-3, used for irradiation of the pressed and sintered pellets is shown in Figure 5. The cast



106-7281

Figure 5. Assembly of Special EBR-I Fuel Rod Used for Irradiation of Pressed and Sintered Carbide Specimens. Two similar fuel rods, without thermocouples, were used for irradiation of the cast specimens.

specimens were irradiated in two similar rods, M-1 and M-2, which did not contain a central thermocouple. Rods M-1 and M-2 each contained four PuC and four UC-PuC specimens. They were arranged so that specimens of each composition were in alternating positions along the length of the fuel rod. All of the specimens in each of the three rods were bonded with NaK to the Type 304 stainless steel cladding. Helium was used as the cover gas over the NaK. Centering of the specimens in the fuel rods was accomplished by placing tantalum spacers on the ends of each specimen.

The three special fuel rods were loaded into subassembly E of the Mark III core. In this location rods M-1 and M-2 were 46 mm (1.82 in.) from the center line of the reactor. The thermocoupled rod M-3 containing the pressed and sintered specimens was 43 mm (1.68 in.) from the center line.

During irradiation, temperatures were measured at various points along the center line of rod M-3. Adjacent temperatures were also measured in the NaK coolant flowing past the fuel rod. From the temperature differences thus determined, and from previously determined plutonium fission rate contours in the EBR-I core,[8] it was possible to calculate the temperatures of the specimens in the two rods which did not contain thermocouples. Corrections were made for the differences in density between the sintered and cast specimens. The assumed thermal conductivities of all specimens were based on preliminary information supplied by British investigators[9] in their studies of the properties of various UC-PuC compositions. Atom burnups in all specimens were calculated from previously determined plutonium fission rates in EBR-I.

After irradiation the rods were shipped to the hot cells at the Lemont site of Argonne National Laboratory. They were opened in an alpha- and gas-tight box in a high-level gamma cell. An atmosphere of nitrogen was used in the box at all times to avoid fires and oxidation of the specimens.

Since the maximum clad inner surface temperature (350°C) was well below that at which carbon pickup, sensitization, or corrosion might be expected to occur, the detailed postirradiation examination was limited to the carbide specimens themselves.

RESULTS AND DISCUSSION

Cast Specimens

Irradiation conditions and the results of the postirradiation examination for the cast PuC and the UC-PuC specimens are summarized in Tables I and II, respectively. Metal atom burnups ranged from 0.060 to 0.10%, and central temperatures were in the range from 370 to 650°C.

Burnups and temperatures were lower in the specimens containing uranium because of the lower fission cross section of U^{235} relative to Pu^{239}.

Table I

EFFECTS OF IRRADIATION ON CAST PuC SPECIMENS

Specimen No.	C, w/o	Metal Atom Burnup, %	Irradiation Temp, °C		Diameter, mm			Density, g/cm³			Remarks
			Surface	Center	Pre	Post	Change	Pre	Post	Change, %	
M-1-8	5.45	0.076	270	370	7.643	7.648	0.005	13.07	13.16	0.69	Removed whole.
M-2-8	5.78	0.076	270	370	7.670	(a)	-	13.06	12.99	-0.54	Removed in three pieces.
M-1-2	4.94	0.090	370	550	7.714	7.719	0.005	13.32	13.43	0.83	Removed in three pieces.
M-2-2	4.95	0.090	370	550	7.668	(a)	-	13.03	13.24	1.61	Removed in three pieces.
M-1-6	4.93	0.098	340	590	7.696	(a)	-	13.31	(a)	-	Removed in large number of pieces.
M-2-6	4.83	0.098	340	590	7.714	(a)	-	13.32	13.22	-0.76	Removed whole but broke up in handling.
M-1-4	5.17	0.10	370	650	7.691	(a)	-	13.22	13.03	-1.44	Removed in seven pieces.
M-2-4	5.30	0.10	370	650	7.691	(a)	-	13.16	13.09	-0.53	Removed in two pieces.

(a)Condition of specimen did not permit measurement.

Table II

EFFECTS OF IRRADIATION ON CAST UC-PuC SPECIMENS

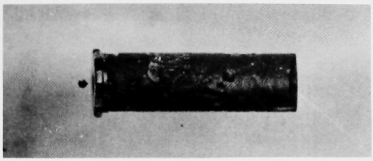
Specimen No.	Pu, w/o	C, w/o	Metal Atom Burnup, %	Irradiation Temp, °C		Diameter, mm			Density, g/cm³			Remarks
				Surface	Center	Pre	Post	Change	Pre	Post	Change, %	
M-1-1	18.2	4.83	0.060	350	390	7.699	7.717	0.018	13.29	13.09	-1.50	Removed whole.
M-2-1	17.2	4.89	0.060	350	390	7.684	7.696	0.012	13.37	13.30	-0.52	Removed in two pieces.
M-1-7	27.6	5.68	0.069	310	490	7.620	7.379	-0.241	13.03	12.92	-0.84	Removed in two pieces.
M-2-7	27.8	5.64	0.069	310	490	7.551	7.653	0.102	13.16	13.08	-0.61	Removed whole.
M-2-3a	25.0	5.16	0.076	360	460	7.470	7.577	0.107	13.30	13.16	-1.05	Removed whole.
M-1-3	18.1	5.50	0.077	360	460	7.549	7.549	0.000	13.18	13.12	-0.46	Removed in two pieces.
M-2-3b	25.0	5.16	0.078	360	460	7.635	(a)	-	13.26	13.26	0.00	Removed whole but broke up in handling.
M-1-5	18.3	4.78	0.079	350	460	7.729	7.719	-0.010	13.35	13.14	-1.57	Removed whole.
M-2-5	18.2	4.75	0.079	350	460	7.699	7.722	0.023	13.23	13.20	-0.23	Removed whole.

(a)Condition of specimen did not permit measurement.

The PuC specimens were observed to have fractured to a greater extent than the mixed-carbide specimens. Typical specimens after irradiation are shown in Figures 6 and 7. The greater amount of fracturing of the PuC specimens may be related to their relatively high content of the brittle plutonium sesquicarbide phase or to generally poor shock resistance of PuC. This behavior might also be the result of the lower thermal conductivity of the PuC phase, which would cause a steeper temperature gradient across these specimens. Such a condition would induce greater stresses in the PuC specimens, which in turn could cause them to fracture. Plutonium-carbon alloys containing the zeta phase have been observed by workers at this Laboratory(4) and at Los Alamos(10) to transform on heating and cooling. Because of the density changes involved, this would also cause thermal stresses. In the present specimens, however, the carbon content was sufficiently high to be outside the range in which zeta formation could occur.

31323 1X

Figure 6. Arc-cast PuC Specimen No. M-1-4 after 0.10 Metal Atom Percent Burnup at a Central Temperature of 650°C. The tantalum end spacers are also shown.



31324 1X

Figure 7. Arc-cast UC-18 w/o PuC Specimen No. M-1-5 after 0.079 Metal Atom Percent Burnup at a Central Temperature of 460°C. A tantalum end spacer is also shown.

Dimensional changes were negligible in the two PuC specimens which could be measured after irradiation. Density changes were both positive and negative, and could not be correlated with composition or irradiation conditions.

In the case of the mixed-carbide specimens, apparent diameter changes as large as 0.24 mm (0.0095 in.) were measured. In view of the poor surfaces of these specimens the indicated dimensional changes are not believed to be significant. Density decreases were observed in all specimens but one, which showed no apparent change. Again, the density changes could not be correlated with composition variables or irradiation conditions. The surfaces of the UC-PuC specimens were generally less bright than those of the PuC specimens.

Attempts to measure fission gas release in the first rod containing cast specimens were unsuccessful because of equipment failure. Measurement of the quantity and composition of the gas in the second rod showed that fission gas release was 0.24% of the theoretical yield. Gas release by surface recoil based on the original surface area of the specimens alone would account for at least 40% of the gas that was measured. With the addition of new surfaces from fuel cracking under irradiation, all the released gas could be accounted for by a recoil-release mechanism. Similar results have been reported by investigators at Harwell.[11]

Pressed and Sintered Specimens

Table III summarizes the irradiation conditions for the pressed and sintered pellets, and the results of the postirradiation examination. Maximum metal atom burnup and irradiation temperature were 0.091% and 380°C, respectively. The fission rate of the sintered pellets was somewhat higher than that of the cast specimens because the pellets were closer to the reactor center line. Temperatures were lower, however, because of the relatively low bulk density of the pellets.

Table III

EFFECTS OF IRRADIATION ON PRESSED AND SINTERED PELLETS OF UC-20 w/o PuC

Specimen No.	Preirradiation Density, % of Theoretical[a]	Metal Atom Burnup, %	Irradiation Temp, °C		Length, mm			Diameter, mm		
			Surface	Center	Pre	Post	Change	Pre	Post	Change
M-3-15	53.3	0.061	250	260	9.20	9.20	0.00	7.920	7.818	-0.102
M-3-14	54.2	0.065	260	270	9.37	9.37	0.00	7.920	7.874	-0.046
M-3-1	57.0	0.066	330	350	20.80	21.12	0.32	7.620	7.721	0.101
M-3-13	55.5	0.072	260	290	12.48	12.48	0.00	7.920	7.971	0.051
M-3-2	57.4	0.077	330	370	22.33	22.72	0.39	7.670	7.684	0.014
M-3-12	52.6	0.077	270	310	12.65	12.05	-0.60	7.920	8.001	0.081
M-3-11	55.7	0.082	280	330	13.10	13.14	0.04	7.920	7.976	0.056
M-3-3	56.3	0.084	320	370	15.92	15.98	0.06	7.640	7.691	0.051
M-3-10	55.5	0.085	290	340	11.59	11.60	0.01	7.920	7.958	0.038
M-3-4	56.3	0.088	320	380	15.85	15.98	0.13	7.640	7.628	-0.012
M-3-9	52.9	0.088	290	350	13.06	13.03	-0.03	8.029	8.098	0.069
M-3-5	55.0	0.090	310	380	15.07	15.07	0.00	7.920	7.920	0.000
M-3-8	54.6	0.090	300	360	11.10	11.13	0.03	7.980	8.000	0.020
M-3-6	56.4	0.091	310	370	9.95	9.97	0.02	7.920	7.932	0.012
M-3-7	53.8	0.091	300	370	11.91	11.95	0.04	8.029	7.950	-0.079

[a]Theoretical density taken as 13.6 g/cm^3. Percent of theoretical based on geometric density after firing.

None of the sintered pellets fractured or developed obvious cracks during irradiation. Although two of the specimens were broken during subsequent handling in the hot cell, they were much more durable than the cast specimens. Length increases up to 0.39 mm (0.015 in.) and diameter increases up to 0.10 mm (0.004 in.) were random. Immersion density measurements were not made with the sintered pellets before or after irradiation because of their extensive open porosity. A typical specimen after irradiation is shown in Figure 8.

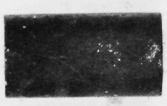


Figure 8

Pressed and Sintered UC-20 w/o PuC Specimen No. M-3-5 after 0.090 Metal Atom Percent Burnup at a Central Temperature of 380°C

EI-555 2X

As might be expected, fission gas release from the pressed and sintered specimens was higher than from the cast specimens because of the large amount of open porosity which existed in the sintered pellets. Table IV shows a comparison of the fission gas release from

Table IV

COMPARATIVE FISSION GAS RELEASE IN RODS CONTAINING ARC-CAST AND PRESSED AND SINTERED SPECIMENS

Rod No.	Type of Specimen	Theoretical Xe Yield cm^3	Released Xe, cm^3	% Xe Released	Theoretical Kr Yield, cm^3	Released Kr, cm^3	% Kr Released	% Total Fission Gas Released
M-1	Cast	(Attempt to collect fission gas was unsuccessful)						
M-2	Cast	1.97	0.004	0.20	0.125	~0.001	~0.8	0.24
M-3	Sintered	1.02	0.115	11.3	0.110	0.021	19.1	12.0

rods M-2 and M-3. In the case of the sintered pellets it was found that 11.3% of the xenon and 19.1% of the krypton was released, giving an overall value for fission gas release of 12.0%. It was possible that either krypton diffused more rapidly than xenon, or that the theoretical yield of krypton used in the calculation is low. Values of the theoretical yields of the isotopes of krypton and xenon were taken from Reference 12.

Sufficient fission gas was available from rod M-3 to obtain a mass spectrographic analysis of the stable xenon and krypton isotopes and of Kr^{85}. The results are listed in Table V. Good agreement was found between actual and predicted xenon isotope ratios. A lack of close agreement is apparent in the krypton data, indicating that the values used for theoretical yields of the krypton isotopes may be in need of adjustment.

Table V

ISOTOPE RATIOS IN THE FISSION GAS RELEASED IN ROD M-3

Isotope	% Present in Total Gas Sample	% of Element	Theoretical Amount, %
Kr^{83}	0.48	17.7	12.7
Kr^{84}	0.75	27.7	21.7
Kr^{85}	0.18	6.6	8.1
Kr^{86}	1.30	48.0	57.5
Totals	2.71	100.0	100.0
Xe^{131}	2.33	15.7	15.5
Xe^{132}	3.22	21.7	21.7
Xe^{134}	4.98	33.5	33.1
Xe^{136}	4.32	29.1	29.7
Totals	14.85	100.0	100.0

CONCLUSIONS

The results of these preliminary irradiations do not indicate any unexpected behavior which might limit the usefulness of either PuC or mixed UC-PuC as a fast reactor fuel. Harwell investigators have recently reported similarly encouraging results with UC-10 w/o PuC.(11) The rather extensive fracturing of the cast PuC is not regarded as being particularly harmful, since ordinarily it would be contained in a ductile cladding as are other brittle ceramic fuels, such as oxide. Additional irradiations of PuC and UC-PuC fuels under more rigorous conditions are in progress at this Laboratory.

ACKNOWLEDGMENTS

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